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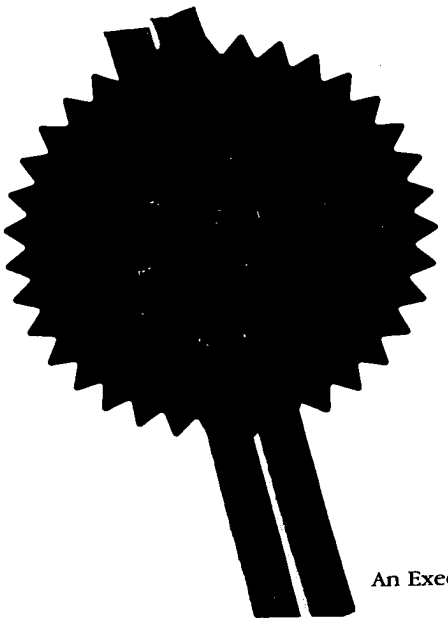

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Dated 18 December 1998

Patents Form 1/77

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Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
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1. Your reference — PB751/iii/GB/RGMS

2. Patent application number *(The Patent Office will fill in this part)* — 03 JUN 1998 **9811778.1**

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

ALBRIGHT & WILSON UK LIMITED
210-222 HAGLEY ROAD WEST
OLDBURY
WEST MIDLANDS
B68 ONN

Patents ADP number *(if you know it)* — 1818002

If the applicant is a corporate body, give the country/state of its incorporation — ENGLAND

4. Title of the invention — BIOCIDAL COMPOSITIONS AND TREATMENTS

5. Name of your agent *(if you have one)* — MR R G M SAVIDGE

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

ALBRIGHT & WILSON UK LIMITED
PATENTS DEPARTMENT
210-222 HAGLEY ROAD WEST
OLDBURY
WEST MIDLANDS
B68 ONN

Patents ADP number *(if you know it)* — 7383219001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*
   a) any applicant named in part 3 is not an inventor, or
   b) there is an inventor who is not named as an applicant, or
   c) any named applicant is a corporate body.
   See note (d))

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	NONE
Description	8 (EIGHT) PAGES
Claim(s)	NONE
Abstract	NONE
Drawing(s)	NONE

10. If you are also filing any of the following, state how many against each item.

Priority documents	NONE
Translations of priority documents	NONE
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	NONE
Request for preliminary examination and search *(Patents Form 9/77)*	NONE
Request for substantive examination *(Patents Form 10/77)*	NONE
Any other documents *(please specify)*	NONE

11. I/We request the grant of a patent on the basis of this application.

Signature

Date 02 July 1998

R G M SAVIDGE, Agent for the Applicant

12. Name and daytime telephone number of person to contact in the United Kingdom

MR R G M SAVIDGE
0121 420 5430

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PATENTS ACT 1977

PRELIMINARY SPECIFICATION

(Description)

BIOCIDAL COMPOSTIONS AND TREATMENTS

Applicant : ALBRIGHT & WILSON UK LIMITED

Inventors :

BIOCIDAL COMPOSITIONS AND TREATMENTS

The present invention relates to synergistic biocidal mixtures of hydroxymethyl phosphonium biocides with certain non-foaming biopenetrants.

GB 2 145 708 describes biocidal uses of tetrakis (hydroxymethyl) phosphonium salts, referred to herein collectively as "THP". US 4 778 813 describes the biocidal use of quaternary ammonium polymers. GB 2 178 960 describes synergism between THP and surfactant. GB 2 228 680 describes synergism between THP and certain aldehydes.

THP formulations are increasingly widely used as biocides for water treatment in treating cooling water, process water e.g. in pulp and paper manufacture, drilling fluids and other aerobic water systems, as well as in anaerobic systems such as oil field formation water, injection water, produced water and water used in hydrostatic testing. Advantages include rapid and effective bactericidal activity and environmental acceptability. Particularly in systems where slime forming bacteria proliferate (e.g. in aerobic systems such as cooling water) it has been found desirable to use THP formulations containing synergistic amounts of a surfactant according to GB 2 178 960, in order to improve cost effective biocidal action. However such formulations cause foaming problems. Attempts to combine THP with other biocides (e.g. aldehydes), which do not cause foaming, have not been able to provide such effective biocidal action against slime forming bacteria, and/or have detracted from the favourable environmental profile of THP.

We have now discovered that combinations of THP with quaternary ammonium polymers and copolymers and/or water soluble glycol ethers, and/or aryl sulphonate formaldehyde copolymers provide strongly synergistic biocidal formulations which give excellent penetration of bacterial slime and improved activity against planktonic bacteria without causing excessive foam.

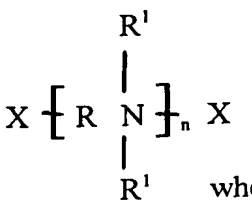
Our invention provides a biocidally synergistic mixture comprising THP and at least one synergist selected from quaternary ammonium polymers and copolymers, water soluble glycol ethers and sulphonated aryl formaldehyde copolymers.

According to a second embodiment the invention provides a method of treating aqueous systems contaminated, or liable to contamination, with bacteria, fungi or algae which comprises applying thereto separately or together a biocidally active amount of the components of a synergistic mixture as aforesaid.

The aqueous system may, for instance, be contaminated with bacterial slime. The invention is of use for treating aerobic systems and also for anaerobic systems.

The THP salt is preferably the sulphate, chloride or phosphate. However any water soluble salt may be used including the nitrate, phosphite, bromide, fluoride, carbonate, acetate, formate, citrate, borate, or silicate. In fact any counter ion which is chemically compatible with the THP cation may be used, the main criteria for selection being economic.

The quaternary ammonium polymer may be any of those described in US 4 778 813. Particularly preferred is poly[oxyethylene(dimethyliminio)ethylene(dimethyliminio)ethylene dichloride]. This is a copolymer of NNN^{1}N^1-tetramethyl-1,2-diamino ethane with bis (2-chloroethyl) ether, which is referred to herein as "WSCP". The latter is the commercial name of the product used in example 1, which is sold by Buckman Laboratories. However any other water soluble polymer containing a plurality of quaternary ammonium groups may be used. Such compounds typically have the formula:



wherein each R is a divalent organic group constituting with the ammonium group a monomeric residue or separately selected from two or more comonomeric residues each R^1 is an alkyl or hydroxy alkyl group, preferably methyl or ethyl, X is hydrogen or a

monovalant inorganic or organic end capping group and n is from 3 to 3000, e.g. 5 to 2000, especially 8 to 1000, e.g. 10 to 500, most preferably 20 to 100.

Some typical examples include:

Poly[hydroxyethylene(dimethyliminio)ethylene(dimethyliminio)methylene dichloride]

Poly[hydroxyethylene(dimethyliminio)-2-hydroxypropylene(dimethyliminio)-methylene dichloride]

N-[3-(dimethylammonio)propyl]-*N*[3-(ethyleneoxyethylenedimethylammonio) propyl]urea dichloride

α-4-[1-tris(2-hydroxyethyl)ammonium chloride-2-butenyl]poly[1-dimethyl-ammonium chloride-2-butenyl]–ω–tris(2-hydroxyethyl)ammonium chloride

The glycol ether is preferably a water soluble compound of the formula $HO[CR_2CR_2O]_nR'$ where each R is methyl, ethyl or preferably H, provided that the total number of carbon atoms per $[CR_2CR_2O]$ group does not exceed 4, more preferably is not more than 3 and most preferably is 2, R' is a lower hydrocarbon group such that the compound is water soluble, e.g. propyl, ethyl or preferably methyl and n is from 1 to 10, especially 1 to 5, typically 1 to 3, preferably 2.

The sulphonated aryl formaldehyde copolymer is preferably sodium naphthalene sulphonate formaldehyde condensate.

The biopenetrant synergist is not usually present in a greater weight concentration than the THP, although higher concentrations by weight based on THP, e.g. up to 10:1 or even 100:1 are technically possible but commercially undesirable. The proportion is preferably less 50% by weight based on the weight of THP, more usually less than 20%, typically less than 10%, especially less than 5%. Although very small amounts may be effective we prefer to use proportions of biopenetrant greater than 0.1% based on the weight of THP, usually greater than 0.5%, especially greater than 1%.

The biocide is typically supplied as a 10 to 75%, e.g. 20 to 60%, especially 30 to 50% by weight aqueous solution of THP containing from 0.1 to 10%, e.g. 0.2 to 5%, especially 0.5 to 2% of the synergist, based on the total weight of the solution.

Alternatively the composition may be supplied as a solid especially a powdery or granular solid coated in an acidic encapsulent such as adipic acid.

The mixture is typically used at a dosage of 1 to 1500ppm by weight THP based on the weight of water to be treated, usually 2 to 500, especially 5 to 250, e.g. 10 to 150.

The invention will be illustrated by the following examples:-

Example 1

THPS/WSCP mixture was compared with two commercial THP/anionic surfactant products for control of legionella pneumophila.

METHODOLOGY

Parameter	Details
Test medium	Sterile WHO Standard hardness water (total hardness 342mg litre^{-1}) plus 3mg litre^{-1} iron as ferric sulphate
Biocides	Stock solutions 10 x the concentration to be tested are prepared in WHO standard hardness water
pH	8.0 0.2
pH adjuster	Boric acid/borax buffer as contained in the test medium
Test organism	*L pneumophila* sg 1 (NCTC 11192)
Test volume	10ml
Contact temp	21 $\pm$ 1^{0}C
Contact times	0, 3, 4 and 6 hours
Inoculum level	To give an initial concentration of approximately 1 x 10^{5} cfu/litre
Preparation of inoculum	Resuscitate test organism from lyophilised culture. Prepare 48h plate culture on BCYE agar. Hold at 4^{0}C overnight. Suspend in 10ml of test medium.
Test method	Add 1ml of biocide stock solution to 8ml of test medium. Control contains 9ml of test medium only. At time 0h add 1ml of inoculum. After the appropriate contact times remove 1ml and make serial 10 x dilutions.
Enumeration method	By performing Miles and Misra dilution counts onto BCYE agar plates.
Replication	Spot 33 micorlitres of each dilution in triplicate onto dry BCYE agar plates to obtain a mean count of surviving legionellae.

Plate incubation temperature	37± 1°C
Plate incubation period	7 days
Expression of results	Give number of control and surviving legionellae and the log 10 reduction in numbers of biocide-treated cell suspensions compare to the appropriate controls.

RESULTS

The results are summarised below

	3 Hour Contact time			4 Hour Contact Time			6 Hour Contact Time		
Product	**25ppm**	**50ppm**	**100ppm**	**25ppm**	**50ppm**	**100ppm**	**25ppm**	**50ppm**	**100ppm**
34% THP 2% anionic surfactant (Comparison A)	1×10^3	6×10^2	1.6×10^3	1.5×10^2	15	ND	30	ND	ND
74% THP 1% anionic surfactant (Comparison B)	6×10^4	4.5×10^2	ND	1.4×10^4	6×10^2	ND	4.5×10^2	ND	ND
50% active THP / 0.7% WSCP (Example)	3×10^3	ND	ND	5.3×10^2	ND	ND	30	ND	ND

Notes: i) ND - Non Detected

ii) The control was 1×10^5

iii) The following conclusions apply:-

- A - Good activity within 4 hours at 50ppm or above
- B - Good activity within 3 hours at 100 ppm or 6 hours at 50ppm
- Example - Good activity within 3 hours at 50 ppm or above

The example of the invention also showed superior performance to conventional THP surfactant formulations, to WSCP alone and to THP alone in reducing planktonic bacteria.

The example gave less than half the foaming observed using surfactant containing formulations.

Example 2

An aqueous solution comprising 50% THPS and 2% WSCP was added to alginate beads infected with sulphate reducing bacteria. When dosed at 250ppm, solution gave a 100 fold reduction in bacterial counts, compared with a control, after two weeks incubation.

At 500ppm the solution gave a total kill.

EXAMPLE 3

An aqueous solution comprising 50% THPS and 2% methyl carbitol (diethylene glycol monomethyl ether) was added to alginate beads infected with sulphate reducing bacteria. When dosed at 250ppm, the solution gave a 100 fold reduction in bacterial counts, compared with a control, after two weeks incubation. A mixture of 50% THP and 2% cationic surfactant was inactive at this concentration. At 500ppm the solution gave a total kill.

The example of the invention also showed superior performance to conventional THP surfactant formulations, to methyl carbitol and to THP alone in controlling both sulphate reducing and planktonic aerobic bacteria.

The example gave less than half the foaming observed using surfactant containing formulations.

The mixture also gives effective control over fungi and algae.

EXAMPLE 4

The alginate bead test of examples 2 and 3 was repeated using sodium naphthalene sulphonate/formaldehyde condensate as the synergist. As 250ppm the solution gave a 100 fold reduction in bacterial counts after two weeks incubation. At 500ppm the solution gave a total kill. The volume of foam generated when air was bubbled through the system containing 750ppm of the active biocidal mixture was half that using THP alone.